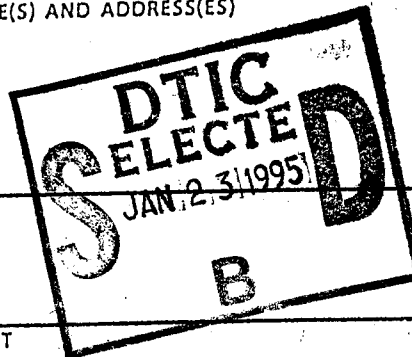


# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 05/00/80		3. REPORT TYPE AND DATES COVERED	
4. TITLE AND SUBTITLE PROGRESS IN DEVELOPMENT ON BASIN F WASTEWATER TREATMENT PROCESSES, PHASE II, TEST RESULTS FROM THE WET OXIDATION PROCESS				5. FUNDING NUMBERS	
6. AUTHOR(S) LAWLESS, H.; SWEDER, R.; LOVEN, C.				8. PERFORMING ORGANIZATION REPORT NUMBER  81320R11	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) ROCKY MOUNTAIN ARSENAL (CO.) COMMERCE CITY, CO				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				11. SUPPLEMENTARY NOTES	
12a. DISTRIBUTION/AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) THE SECOND PHASE OF A SMALL-SCALE INVESTIGATION OF THE SET-OXIDATION REACTION HAS BEEN COMPLETED. THE MAIN OBJECTIVE HAS BEEN TO DEVELOP A PROCESS FOR REMOVING THE ORGANIC MATERIAL, THE COPPER, AND THE FLUORINE IN SOLUTION IN BASIN F WASTE SO THAT A RELATIVELY NONTOXIC PRODUCT WILL REMAIN FOR EITHER SECONDARY TREATMENT OR POSSIBLY DIRECT DISPOSAL. A CONTINUOUSLY - FED, AGITATED REACTOR WAS USED FOR SEVERAL RUNS, AS AN APPROXIMATION TO A FULL-SIZE PLANT. THE OVERALL OBJECTIVES OF THIS SECOND PHASE OF THE TEST PROGRAM WERE TO CONFIRM THE INITIAL TEST RESULTS AND TO PROVIDE A PRELIMINARY ESTIMATE OF THE SIZE OF A FULL-SCALE, CONTINUOUS-FLOW PLANT. AT THE SAME TIME, AN ATTEMPT WAS MADE TO EVALUATE THE OXIDATION-RATE EFFECTS OF PH, RESIDENCE TIME, AND CATALYST. A SECONDARY OBJECTIVE WAS TO START THE DEVELOPMENT OF A MATHEMATICAL MODEL OF THE WET OXIDATION OF BASIN F LIQUID SO THAT, AFTER REFINEMENT, THE MODEL WILL BE AVAILABLE TO PROVIDE ENGINEERING DATA.					
14. SUBJECT TERMS PESTICIDES; CONTAMINATION, ORGANIC COMPOUNDS				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION UNCLASSIFIED		18. SECURITY CLASSIFICATION OF THIS PAGE		19. SECURITY CLASSIFICATION OF ABSTRACT	
				20. LIMITATION OF ABSTRACT	



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PROGRESS IN DEVELOPMENT OF BASIN F WASTEWATER  
TREATMENT PROCESSES

PHASE II - TEST RESULTS FROM THE WET OXIDATION  
PROCESS

Rocky Mountain Arsenal  
Information Center  
Commerce City, Colorado

by

PROCESS DEVELOPMENT AND EVALUATION BRANCH  
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REPORT NO. 2

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PROGRESS IN DEVELOPMENT OF BASIN F WASTEWATER TREATMENT  
PROCESSES - PHASE II

1. Summary and Conclusions

1.1 The second phase of a small-scale investigation of the wet-oxidation reaction has been completed. The objective has been to develop a process for removing the organic material, the copper, and the fluorine in solution in Basin F waste so that a relatively nontoxic product will remain for either secondary treatment or possibly direct disposal. A continuously-fed, agitated reactor was used for several runs, as an approximation to a full-size plant.

1.2 Several combinations of the reaction variables were tested, and the best combination removed 95 percent or more of both the oxidizable carbon and the copper. Fluorine removal would require a second step but was not tested at this time because comparatively large samples would have been needed. Fluorine is being routinely removed from groundwater in operations now in progress at RMA; the process should also work for the wet-oxidation product.

1.3 Equations that comprise a preliminary mathematical model of the wet-oxidation reaction in both the continuous-flow and the batch reactors were developed and were used to obtain preliminary estimates of the oxidation rate constant. Although these estimates are not accurate enough to constitute engineering data, they were used to derive a preliminary estimate of the size of a full-scale reactor. Further refinement of the equations will be required in order to produce engineering data, but a full-scale reactor that would be capable of processing all the Basin F liquid within a three-year operating period appears to be feasible. These preliminary estimates call for a sequence of between four and six stages, each with a volume between about 500 gallons and about 1,500 gallons. The temperature and pressure required would be approximately 600°F and 2,000 psi. An oxidation level of 98 percent was projected.

1.4 Continued investigation of the wet-oxidation process is recommended. Experiments should be conducted under local control so that the process can be modeled accurately.

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PROGRESS IN DEVELOPMENT OF BASIN F WASTEWATER TREATMENT PROCESSES -  
PHASE II - Cont

2. Introduction

2.1 The waste liquid in Basin F has accumulated from various manufacturing operations carried out in the past at RMA. Reference 3, Table 2, contains the best recent analysis of the liquid. The Total Oxidizable Carbon (TOC) in solution is about 2 percent of the liquid. These organic compounds plus about 700 ppm copper and about 115 ppm fluorine account for most of the environmentally-damaging character of the waste. Because of the high concentration of toxic compounds in the Basin F liquid, one part of this liquid has the potential for contaminating several hundred to several thousand parts of groundwater, depending on the allowable levels for a given compound.

2.2 Wet-oxidation is one of the processes now under investigation at RMA in connection with detoxification of the Basin F liquid. By this process, at temperatures from about 550°F to 700°F, in the presence of liquid water, most nonvolatile organic compounds can be oxidized to carbon dioxide and water. Atoms other than carbon and hydrogen appear in the product as inorganic compounds. One preliminary process-test result is listed in Reference 1; the result was encouraging enough to justify the Phase II test plan outlined in Reference 2. This report is comprised of the Phase II test results.

2.3 At their original concentration of about 2 percent, the organics in Basin F liquid are much too concentrated for economical removal by adsorptive processes. After wet-oxidation, the disposal of treated Basin F liquid is expected to become economically feasible either with adsorptive processing or possibly without further treatment. Wet-oxidation reduces toxicity by removing both the organic compounds and copper. A fluoride removal process that is expected to suit the wet-oxidation product is being operated currently at RMA. Disposal of the low-toxicity waste which also has a low oxygen demand is expected to be simple, compared to disposal of the raw waste or to its indefinite retention in Basin F.

2.4 The objectives of this second phase of the test program were to confirm the initial test results and to provide a preliminary estimate of the size of a full-scale, continuous-flow plant. At the same time, an attempt was made to evaluate the oxidation-rate effects of pH, residence time, and catalyst. A secondary objective was to start the development of a mathematical model of the wet oxidation of Basin F liquid so that, after refinement, the model will be available to provide engineering data.

PROGRESS IN DEVELOPMENT OF BASIN F WASTEWATER TREATMENT PROCESSES -  
PHASE II - Cont

3. Experimental

3.1 See Figure 1 for a diagram of the experimental design. All runs were carried out by ASTRO Metallurgical Corporation, Wooster, Ohio. Some of the runs departed from the design because of unpredictable experimental problems. High corrosion rates prevented runs at pH 3 and caused considerable corrosive damage to the tantalum reactor. Accordingly, no data was obtained from Runs 4 and 10 (Figure I) beyond that regarding the corrosion damage.

3.2 The continuous-flow runs with catalyst were cancelled in favor of two batch runs when it was found that the platinum catalyst had been lost during Run 8. Runs 6, 7, and 8 were replaced by one batch run because they differed only in feed rate. Run 9 was replaced by the second batch run. Catalyst effectiveness was measured equally as well by batch as by continuous-flow runs.

3.3 The above exceptions to the experimental program were not caused by fundamental limitations in the wet-oxidation process.

3.4 The experiments were conducted as described below:

3.4.1 Process Charge Stock - The feed stock for all runs was taken from the same master sample of Basin F waste liquid that was obtained about Jun 78.

3.4.2 Adjustment of pH - Solid caustic was used to adjust the waste from its normal pH of 7 to pH 11. The change in organics concentration was thus minimized. The low pH runs were abandoned for reasons given above.

3.4.3 Chemical Analyses - Samples were analyzed at RMA (Environmental Division, Analytical Systems Branch). Some TOC and COD (Chemical Oxygen Demand) analyses were provided by the contractor.

3.4.4 Reactor - A continuously-fed, stirred reactor of two gallons capacity was used for the continuous-through-put runs. Preliminary calculations (Reference 2) had indicated that, for all the experimental runs, a stable product composition would be reached after five hours run time or less. Accordingly, small samples were collected at intervals up to five hours, and a large, five-gallon sample was produced after the five hour period, when the product composition had stabilized. Where continuous-flow runs were not practical (catalyst loss), batch reactions were substituted.

PROGRESS IN DEVELOPMENT OF BASIN F WASTEWATER TREATMENT PROCESSES -  
PHASE II - Cont

3.5 Experimental Design

3.5.1 Independent variables are those under the control of the experimenter. As represented in Figure I, this design included: (1) Flow rate (or residence time), (2) pH of the waste liquid, and (3) The presence of a catalyst, as independent variables.

3.5.2 The dependent variables are those that are measured:

3.5.2.1 TOC was chosen as a measure of the oxidative load on the environment that would be caused by disposal of the product. Since TOC reflects the concentration of organics in the product, it can be expected to also provide a rough measure of the toxicity of the product.

3.5.2.2 Copper (Cu) is toxic to both aquatic life and mammals. Its level is an important measure of the quality of the treatment process.

3.5.2.3 Specific organics were measured as an indication of the reduction in toxicity. A profile consisting of the levels of ten compounds, particularly pesticides and their intermediates, was used for comparison of the treated and untreated waste liquid.

3.5.3 Parameters are factors which are constant. In this case, it was known that the maximum practical temperature was the desirable level, so the temperature was fixed as a parameter. The pressure in the reactor is largely determined by its temperature.

3.5.4 The experimental design represented in Figure I is a partial factorial design that is particularly suitable for statistical analysis. However, in this instance, the experimental difficulties have caused some of the data to be lost and have prevented a meaningful analysis. This is the major reason why future experiments should be conducted under local control. It isn't feasible to cover all contingencies in a contract for experimental work of any degree of complexity.

3.6 Glossary - As an adjunct to Table VII, a glossary of the organic compounds described in item 3.5.2.3 above has been provided.

3.7 Data Analysis - The oxidation rate of the waste is an important factor in estimating the practicability of a large-scale wet-oxidation process. Equations that represent the reaction kinetics in a simplified manner have been used as a means of obtaining first approximations to the rate constant for wet oxidation of the Basin F waste at 600°F.

PROGRESS IN DEVELOPMENT OF BASIN F WASTEWATER TREATMENT PROCESSES -  
PHASE II - Cont

3.7.1 As summarized in Appendix B, equation B-I describes the change in product composition as run-time in a continuous-flow reactor increases. A first-order reaction is assumed. This relation was used to estimate K (the rate constant) during Runs 1, 2, 3, and 5, before and after the product composition had stabilized. For the batch runs, K was estimated from equation B-II.

3.8 Engineering Estimates - Although the rate-constant estimates that were obtained are not accurate enough for any construction purpose, preliminary calculations of the size of a full-scale plant were based on the constant, as a rough indication of the practicability of the wet-oxidation process. The assumptions involved and the results of the calculations are summarized in Appendix A.

#### 4.0 Discussion

4.1 The TOC is a measure of the organic content of the Basin F wastewater. Accordingly, TOC removal becomes a useful measure of the value of a process for treatment of the waste. The reduction in TOC is a direct measure of the reduction of the oxidative load that would otherwise be imposed by disposal into a surface stream; TOC is comparable to Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD), as an indicator of process quality. TOC is also an indicator of the toxicity of Basin F waste because much of the toxicity is due to organic compounds in solution.

4.1.1 In addition to TOC, an estimate of the reduction in toxicity can be obtained by comparing the levels of pesticides, pesticide by-products, and intermediates in the processed waste with their original levels in Basin F (Table VII).

4.1.2 The wet oxidation process was carried out under the reaction conditions shown in Figure I. The reduction in TOC is shown in Tables I, III, and V. Although there are inconsistencies in the data, over 95 percent of the TOC was removed under the best oxidation conditions (Table VI).

4.2 The rate of oxidation is necessary information for estimating the reactor size for a full-scale plant. Values for K, the oxidation rate constant, were calculated from the analytical data, using the appropriate formula (Appendix B). Results obtained are tabulated in Tables II, III, and V. More runs will be necessary to develop an accurate value for K, but the batch runs indicate that 0.04 is a rough approximation for a temperature of 600°F. It is at least a far better value than any available prior to these runs.

PROGRESS IN DEVELOPMENT OF BASIN F WASTEWATER TREATMENT PROCESSES -  
PHASE II - Cont

4.2.1 Using  $K = .04$ , the calculations outlined in Appendix A lead to an estimate of between four and six reactor stages, each having between 460 and 1,380 gallons capacity. The conversion is assumed to be 50 percent at each stage, and the feed rate is assumed to lie between 23 and 69 gpm, in order to process a range of 100 to 300 acre feet of liquid waste within a three-year period.

4.2.2 Different assumptions lead to different results, but the process can probably be carried out in a plant of reasonable size (and cost). Further data will provide better accuracy and reliability for this estimate, and will permit the use of cost data in the design.

4.3 In addition to the toxicity associated with the dissolved organics in Basin F waste, the existing level of dissolved copper is extremely toxic (about 700 ppm, Reference 3). Data from the wet-oxidation process leads to the expectation that all copper can be removed (Tables I and VI).

4.3.1 Rate constants for copper oxidation were calculated (Table IV), but more data will be necessary to obtain reliable values. The oxidation was assumed to be first order, and the calculation methods in Appendix B were applied.

4.3.2 It is clear that substantial amounts of the copper were removed via oxidation, but there were unidentified factors that affected the results. There was substantial loss of copper during the preheating phase, Runs 1 and 2 appeared to have more copper in the product after five hours run time than after three hours. It will be necessary to work with the reaction under local control until self-consistent results can be obtained.

## 5.0 Conclusions and Future Work

5.1 Present indications are that the wet-oxidation process is capable of removing 95 percent or more of the organic material and copper in Basin F waste liquid. Pesticide residues were also reduced to extremely low levels. More bench-scale experiments should be carried out so that necessary engineering data for a pilot unit can be developed. From preliminary data, the size of a full-scale unit will be reasonable.



PROGRESS IN DEVELOPMENT OF BASIN F WASTEWATER TREATMENT PROCESSES -  
PHASE II - Cont

5.2 Disposal of the wet-oxidation product is expected to be greatly simplified, with respect to the raw waste. Biological assays will be necessary during the next phase, in order to quantify this estimate. If necessary, secondary and tertiary treatment can be employed. For example, the low TOC levels should allow further purification via carbon adsorption treatment of the wet-oxidation product.

5.2.1 In regard to conventional sewage at RMA, which may contain detectable levels of toxic chemicals, the wet-oxidation process was originally developed for treatment of such sewage, and treatment of a combined stream of conventional and Basin F waste might provide a means of diluting the inorganic salts in Basin F for disposal.

5.3 The preliminary mathematical modeling of the wet oxidation reaction has provided as basis for estimating the size of a full-scale plant, although there is a large uncertainty involved. A full-scale plant capable of high oxidation (conversion) levels (about 95 percent) will require several sequential stages of wet oxidation. This design will minimize the size and cost of the high-pressure vessels, as compared to a single-stage plant. Although this estimate is too uncertain to be very useful, the full-scale plant will probably have four to six sequential stages of 500 to 1,500 gallons capacity.

5.3.1 Development of the mathematical model should be continued to the point where it will eventually provide engineering data that is accurate enough for plant design. Cost data should be introduced as soon as acceptable accuracy has been obtained with respect to the chemistry.

5.4 Future experimental work should be conducted at RMA so that all variables can be identified and included in the model.

5.5 The simultaneous removal of dissolved organics and of copper content, which was found to occur during the wet-oxidation process, would be expected to cause a great reduction in toxicity of the product as compared to the original Basin F waste. Provision for bioassay of the product should be included in future experiments.

5.6 The platinum catalyst had no marked effect on the wet-oxidation rate. Some other catalysts are described in the literature and are represented as allowing wet oxidation at comparatively low temperatures. Plant operation

PROGRESS IN DEVELOPMENT OF BASIN F WASTEWATER TREATMENT PROCESSES -  
PHASE II - Cont

costs are smaller at lower temperatures, and future work should include investigation of these catalysts.

5.7 The pH of the wastewater feed to the wet-oxidation reaction appears to have no significant effect on the oxidation rate, in the range of 7 to 11. At pH 3, the corrosion rate was much too high for practical operation. This information indicates that the charge stock should be treated at its original pH of 7 and that no expensive pretreatment of the wastewater will be required.

6. References

- a. Lawless, H. L., "Preliminary Test of the Wet Oxidation of Organics in Basin F Wastewater, Report No. 1," Apr 78. 81335R01
- b. Lawless, H. L., "Phase II Testing of the Wet Oxidation of Organics in Basin F Wastewater," Jul 78.
- c. Buhts, Robert E., CPT; Francingues, Norman R., and Green, Andrew J., "Miscellaneous Paper EL-79, Basin F, Investigative Studies, Report 1, Chemical Assessment and Survey," Jun 79.

TABLE I

Factorial Design - Basin F Wet Oxidation Runs.

All runs on Basin F waste at 600°F  
Continuous feed to stirred reactor.  
Run conditions are nominal values

Feed Rates to Two Gallon Reactor	No Catalyst			Trial Catalyst		
	pH=3	pH=7	pH=11	pH=3	pH=7	pH=11
		Run 1			Run 8	
G=0.4 gph						
G=1.0 gph	Run 4	Run 2	Run 5	Run 10	Run 7	Run 9
G=4.0 gph		Run 3			Run 6	

Note: (1) Due to unacceptable corrosion rates, Runs 4 and 10 at pH 3 were cancelled.

(2) Catalyst losses caused runs 6,7,8, and 9 to be cancelled. Two batch runs were substituted, one at pH 7 and the second at pH 11.

TABLE I - CONTINUOUS FLOW WET OXIDATION  
(RUNS 1, 2, 3, & 5)

TOC (Total oxidizable carbon) and Cu (Copper) removal as obtained during Phase II tests of the wet oxidation process for detoxification of Basin F waste water. All runs were continuously fed at 600°F and 2,000 psi, without catalyst; test reactor volume was two gallons.

Aqueous pH	7	7	7	11
Feed (gpm)	.4	1	4	1
Run No.	1	2	3	5
TOC (ppm) Cold, 0 min	13,600	13,050	-	14,100
Hot, 0 min	4,210	5,910	-	-
30 min	5,310	166	-	-
90 min	6,620	82	-	-
180 min	6,830	102	-	-
300 min	543	-	-	-
Steady State	521	580	4,210	240
Cu (ppm) Cold, 0 min	685	1,040	-	635
Hot, 0 min	442	59	-	-
30 min	333	8	-	-
90 min	.6	5	-	-
180 min	.8	38	-	-
300 min	1.6	-	-	-
Steady State	2.6	310	800	44.4

Conclusions:

- (1) The removal of both TOC and Cu is nearly complete under the best reaction conditions.
- (2) Some unidentified factors are causing erratic results. Suspect dilution and/or evaporation in different parts of the apparatus. Further tests should be done under local control

NOTE: See Tables II, III, IV, and V for rate constant estimates from this data and from two batch runs.

TABLE II - CONTINUOUS FLOW WET OXIDATION \*

Estimation of K (rate constant for wet oxidation) from the continuous-feed reaction model, as applied to ASTRO Corporation data for TOC (Table I)

Run Time (Min)	Existing pH in Basin F (pH = 7)						pH = 11	
	Run 1		Run 2		Run 3		Run 5	
	TOC ppm	K Min <sup>-1</sup>	TOC ppm	K Min <sup>-1</sup>	TOC ppm	K Min <sup>-1</sup>	TOC ppm	K Min <sup>-1</sup>
0 (Cold)	13,600	-	13,050	-	-	-	14,100	-
0 (Hot)	4,210	-	5,910	-	(5,085) **	-	(5,085) **	-
30	5,310	-	166	.290	-	-	-	-
90	6,620	-	182	.262	-	-	-	-
180	6,830	-	102	.474	-	-	-	-
300	543	.023	-	-	-	-	-	-
Product	521	.024	580	.077	4,210	.007	240	.767

#### Conclusions:

- (1) The 0 (Hot) TOC data was used as the feed composition. There is a need for experiments in local facilities to explain the TOC reduction during preheating.
- (2) The TOC losses during preheat make the data unsuitable for rate calculations, but the computer program gave reasonable magnitudes for K.
- (3) See Table VI for percentage removals of TOC and Copper.

\* All runs were made in a continuously-fed 2 gallon reactor at 2,000 psi and 600°F, without catalyst.

\*\* Data in parenthesis is the average from Runs 1 and 2; all runs used the same feed.

NOTE: See Appendix B for equation B-1A used to deduce K.

TABLE III - BATCH WET OXIDATION  
(RUNS 6, 7, & 8) \*

Estimation of K (rate constant for wet oxidation) from TOC (total oxidizable carbon) and COD (chemical oxygen demand) data from batch run at 600°F, pH 7, and 2,000 psi, with platinum catalyst.

Run (Min)	COD (ppm)	K (COD) (Min <sup>-1</sup> )	TOC (ppm)	K (TOC) (Min <sup>-1</sup> )
0	34,604	-	13,500	-
3	-	-	4,924	.34
6	-	-	3,822	.08
12	11,312	.09	3,188	.03
30	7,861	.02	2,386	.02
60	6,551	.01	1,794	.01

The above estimates of K are based on equation B-II, Appendix B.

Conclusions:

- (1) The trends in the value of K indicate that a more complex reaction model is required. Experimental errors would be random. The above trends show a departure from equation B-II, Appendix B.
- (2) A good TOC removal of 87 percent in one hour was obtained.
- (3) The reaction kinetics are not greatly affected by this catalyst. Comparable K values were found in the preliminary batch run without catalyst. (Reference 9a, page 6.)

\* This batch run replaces continuous-fed Runs 6, 7, and 8 -- see text.

TABLE IV - CONTINUOUS-FLOW WET OXIDATION

Estimation of  $K'$  (rate constant for Copper oxidation) from ASTRO Corporation wet oxidation runs on Basin F wastewater (see Table I).

Run Time (Min)	Existing pH in Basin F (pH = 7)						pH = 11	
	Run 1		Run 2		Run 3		Run 5	
	Cu ppm	$K'$ Min <sup>-1</sup>	Cu ppm	$K'$ Min <sup>-1</sup>	Cu ppm	$K'$ Min <sup>-1</sup>	Cu ppm	$K'$ Min <sup>-1</sup>
0 (Cold)	685	-	1,040	-	(837) *	-	635	-
0 (Hot)	442	-	59	-	-	-	-	-
30	333	.01	8	-	-	-	-	-
90	.6	2.45	5	-	-	-	-	-
180	.8	1.84	38	-	-	-	-	-
300	1.6	.91	-	-	-	-	-	-
Product	2.6	0.56	310	.02	800	-	44	0.11

\* Average of Runs 1 and 2.

NOTE: See Appendix B for equation used to deduce  $K'$ .

Conclusions:

- (1) Essentially, all the Copper was removed. This feature of the process will prevent Copper toxicity; and accordingly, simplify disposal of the wet oxidation process product. At this time, Copper recovery is uncertain.
- (2) The estimates of the rate constant are affected by the unexpected oxidation during preheat. The initial analysis is also erratic, indicating that some unrecognized variables have affected them.
- (3) Further experiments are needed to obtain controlled data and to check Copper recovery possibilities.

TABLE V - BATCH WET-OXIDATION (RUN 9)

Estimation of K (rate constant for wet oxidation) from COD (Chemical Oxygen Demand) and TOC (Total Oxidizable Carbon) from batch run at 600°F, pH 12, and 2,000 psig, with platinum catalyst.

Run (Min)	COD (ppm)	K (COD) (Min <sup>-1</sup> )	TOC (ppm)	K (TOC) (Min <sup>-1</sup> )
0	35,000	-	14,574	-
3	-	-	3,809	.45
6	7,797	.25	3,495	.03
12	7,580	.05	3,052	.02
30	5,847	.01	2,157	.02
60	5,414	.00	1,808	.01

The above estimates of K are based on equation B-II, Appendix B.

Conclusions:

- (1) Compared to the batch run at pH 7, higher pH does not affect the oxidation rate.
- (2) The platinum catalyst does not appear to change the oxidation rate, but cheaper catalysts should be checked, in view of potential effects on plant cost.



TABLE VI - REDUCTION OF TOC (TOTAL OXIDIZABLE CARBON) AND  
Cu (COPPER) OBTAINED UNDER VARIOUS REACTION  
CONDITIONS

Run Time (Min)	Percent of Initial TOC in Product					
	Run 1 Cont Fed	Run 2 Cont Fed	Run 3 Cont Fed	Run 5 Cont Fed	Run 6, 7 & 8 Batch	Run 8 Batch
(Cold) 0	100	100	100	100	100	100
(Hot) 0	31	45	-	-	36	26
30	39	1	-	-	28	24
90	48	1	-	-	24	21
180	50	1	-	-	18	15
300	4	-	-	-	13	12
Steady State	4	4	31	2	-	-

Run Time (Min)	Percent of Initial Copper in Prod			
	1	2	3	5
(Cold) 0	100	100	100	100
(Hot) 0	64	6	-	-
30	49	1	-	-
90	-	0	-	-
180	0	4	-	-
300	0	-	-	-
Steady State	0	29	100	7

Conclusions:

- (1) Very high removal of TOC and Copper was obtained under the best reaction conditions.
- (2) Further experiments under local control will be necessary in order to resolve inconsistencies in this data.
- (3) The zero-time data for both TOC and Cu indicates premature introduction of air.

NOTE: Batch runs sampled at 3, 6, 12, 30, and 60 min. Run times do not apply to batch runs. See Figure I for run conditions.

TABLE VII

IMPROVEMENT OF CONTAMINANT PROFILES DUE TO WET OXIDATION OF LAKE F  
WASTE UNDER VARIOUS REACTION CONDITIONS

	Analyses of Lake F Waste (ppb)					Unprocessed		
	After Wet Oxidation					Samples from Lake F as of the year shown (1973) (1977) (1979)		
Res Time (Hr) pH of Feed GPM Feed Rate	Run 1	Run 2	Run 3	Run 5				
	5	2	.5	2				
	7	7	7	11				
	.4	1	4	1				
Contaminants *								
Aldrin	< 1	< 1	< 1	5.5	2,064	81	205	
CPMO <sub>2</sub>	556	11,500	< 5	-	-	-	48,000	
CPMSO	73	< 5	< 5	-	-	-	5,900	
DIMP	< 2	< 2	< 2	3.5	-	6,000	18,000	
Dithiane	< 5	< 5	34.7	-	-	88	54	
Dieldrin	< 0.5	< 0.5	< 0.5	< 0.5	1,748	14	44	
Endrin	< 0.5	< 0.5	< 0.5	< 0.5	178	7	21	
Isodrin	< 0.5	< 0.5	< 0.5	< 0.5	-	3	6	
Oxathiane	< 5	< 5	< 5	-	-	20	-	
PCPMS	< 5	< 5	< 5	-	-	-	-	

\* See Glossary

Conclusions: Wet oxidation at 600°F and 2,000 psi removes a broad spectrum of the contaminants present in the waste water stored in Lake F. Possibly the toxicity can be sufficiently reduced to allow discharge into surface streams. The next test phase should include biological toxicity tests.

GLOSSARY - TABLE VII

D IMP	DIISOPROPYLMETHYLPHOSPHONATE
DMMP	DIMETHYLMETHYLPHOSPHONATE
TMP	TRIMETHYLPHOSPHITE
CPMSO	p-CHLOROPHENYLMETHYLSULFOXIDE
CPMO <sub>2</sub>	p-CHLOROPHENYLMETHYLSULFONE
DITH	DITHIANE
OXAT	OXATHIANE
DCPD	DICYCLOPENTADIENE

PESTICIDE TRADE NAMES

ALDRIN, ENDRIN, DIELDRIN, ISODRIN, pp'DDT, and pp'DDE. PCPMS represents NEMAGON

## APPENDIX A

### ESTIMATION OF THE SIZE OF A FULL SCALE REACTOR FOR TREATMENT OF BASIN F WASTE WATER BY THE WET-OXIDATION PROCESS

Two assumptions were employed as basis for the estimate:

- (1) Basin F plus other possible sources have a total volume between 100 and 300 acre-feet.
- (2) A continuous process will operate for three years at 90% stream factor  
The required feed rates are 23, 46, and 69 gpm to process 100, 200, and 300 acre-feet in three years.

The following equation applies to a single stage at steady state:

$$(AI) \quad V = \frac{G}{K} \left[ \frac{B_i}{100 - B_i} \right]$$

Where: G = flow-through rate (gpm) = feed rate

K = Rate constant ( $\text{min}^{-1}$ )

$B_i$  = Conversion of the waste in the feed, percent of the maximum possible conversion (oxidation).

V = Volume of the reaction stage (gals)

For the case where N sequential stages are employed (to minimize the reactor volume necessary to reach a given conversion level) :

$$(AII) \quad \frac{B_T}{100} = 1 - \left( 1 - \frac{B_i}{100} \right)^N$$

Where:  $B_T$  = The total conversion obtained from N sequential stages.

$B_i$  = The conversion obtained in each of the N individual stages.

# APPENDIX A

## TABLE A-1

SOLUTIONS OF EQUATION AI FOR V \*

<u>REACTOR THROUGHPUT</u>	<u>B<sub>i</sub> = 50</u>	<u>B<sub>i</sub> = 75</u>	<u>B<sub>i</sub> = 90</u>
23 gpm	460	1380	4140
46 gpm	920	2760	8280
69 gpm	1380	4140	12420

\* K has been approximated at .05

From Table A-1, the reactor volume that would be needed for high conversion levels in one stage is impractibly large. Some number of sequential stages will be required, as calculated via AII.

## TABLE A-2

SOLUTIONS OF EQUATION AII FOR B<sub>T</sub>

<u>THE TOTAL NUMBER OF STAGES</u>	<u>B<sub>i</sub> = 50</u>	<u>B<sub>i</sub> = 75</u>	<u>B<sub>i</sub> = 90</u>
N = 1	50.00	75.00	90.00
2	75.00	93.75	99.00
3	87.50	98.44	99.90
4	93.75	99.61	--
5	96.88	99.90	--
6	98.44	--	--
7	99.22	99.99	100.00

Conclusion: From the above tables, between 4 and 7 stages with B<sub>i</sub> = 50% or so conversion at each stage would give between 94% and 99% conversion. Each stage would be between 460 gallons and 1380 gallons volume, depending primarily on

## APPENDIX A

the actual number of acre-feet to be processed and the true oxidation rate constant.

These are very uncertain estimates because of the limited basis. More experimental data is needed.

## APPENDIX B

Equation B-I below describes the case where a first-order reaction is carried out in a stirred reactor of constant volume with continuous throughput. The actual wet-oxidation reaction is only approximated by this model.

### Definitions:

$C$  = concentration of reactant (oxidizable carbon) in the product  
(and inside the reactor).

$C_0$  = Concentration of reactant in the feed stock.

$R = C/C_0$

$K$  = First order rate constant ( $\text{min}^{-1}$ )

$G$  = Feed flow rate (gpm).

$V$  = Reactor Volume (gallons)

$t$  = Run time (min) measured from the time the feed starts to a preheated reactor that is filled with feed material at reaction temperature. The feed and the reaction start simultaneously

### Equation:

Equation BI describes the change in product composition as time progresses from zero at the start of the feed.

$$(BI) \quad R = \frac{G + KV e^{-(K + \frac{G}{V})t}}{G + KV}$$

To deduce  $K$  from the reactor data for continuous flow operation, (BI) is transformed to:

$$(BIA) \quad K = \frac{G(1-R)}{V[A - e^{-(K + \frac{G}{V})t}]}$$

A trial-and-error solution for BIA has been programmed for the HP97 calculator.  $K$  values in Tables III and IV were obtained from the experimental data via the HP97 program, for the continuous-feed runs. Batch runs were represented by equation BII:

(BII)  $\ln\left(\frac{1}{x}\right) = Kt$

The above approximations to the wet-oxidation kinetics need to be refined into a more accurate representation of the reaction, but they have provided a preliminary estimate of the size of a full scale reactor (Appendix A) that appears to be reasonable.